CORROSION INHIBITION OF MILD STEEL IN HYDROCHLORIC ACID SOLUTIONS BY THE EXTRACT OF *NYPA FRUTICANS WURMB*

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ABSTRACT

This study assesses the corrosion inhibition effect of the leaves of Nypa Fruticans Wurmb on the corrosion of mild steel in hydrochloric acid medium. The inhibition performance of this natural corrosion inhibitor was determined in certain condition. The inhibitor was prepared by extraction of Nypa Fruticans leaves and the solutions was prepared according to different concentration of the inhibitor and concentration of HCl. Weight loss study on mild steel was performed in order to find the inhibition efficiency (I.E%). Result from this study shows that the inhibition performance of Nypa Fruticans Wurmb is high at high concentration of the inhibitor. However, the concentration of HCl solution did not influence the inhibition efficiency. Nypa Fruticans inhibitor has great potential to be use in industries related with piping system as a clean, safe, and economic corrosion inhibitor.

ABSTRAK

Kajian ini adalah berkenaan tentang kesan perencat hakisan daripada daun pokok nipah keatas kadar hakisan keluli lembut di dalam larutan asid hidroklorik. Prestasi rencatan perencat semula jadi ini akan ditentukan dalam beberapa keadaan. Perencat disediakan daripada ekstrak daun pokok nipah dan larutan disediakan berdasarkan perbezaan kepekatan perencat dan juga berdasarkan pada kadar perbezaan kepekatan HCl. Kajian penurunan berat keluli lembut telah dilakukan untuk mencari kadar peratusan keberkesanan rencatan. Keputusan dari kajian ini mendapati, kadar peratusan keberkesanan rencatan ekstrak daun pokok nipah adalah tinggi dalam keadaan kepekatan perencat yang tinggi. Walau bagaimanapun, kajian ini mendapati kadar peratusan keberkesanan rencatan tidak dapat dipengaruhi oleh kadar kepekatan HCl. Oleh itu, kajian ini mendapati perencat daun nipah mempunyai potensi yang besar untuk digunakan dalam industri yang berkait rapat dengan sistem perpaipan sebagai perencat hakisan yang bersih, selamat, dan juga menjimatkan.

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LIST OF ABBREVIATIONS

PGU	Peninsular Gas Utilization
PGB	Petronas Gas Berhad
TOD	Transmission Operating Division
Bcf/d	Billion cubic feet per day
%E	Percentage of efficiencies
HSNO act	Hazardous Substance and New Organism act
DPC	1,5 Diphenyl Carbazone
HCl	Hydrochloric Acid
ASTM	American Society of Testing Materials
W_i	Initial weight of coupon
W_f	Final weight of coupon
I.E%	Percentage of Inhibition Efficiencies
OCP	Open Circuit Potential
GCMS	Gas Chromatograph Mass Spectrometry

1 INTRODUCTION

1.1 Research Background

Nypa Fruticans or commonly known as the nipa palm is a species of palm native to the coastlines and estuarine habitats of the Indian and Pacific Oceans. It is the only palm that adapted to the mangrove environment. Nypa Fruticans has trunk that grows beneath the ground and only the leaves and flower stalk upwards above the surface. It is highly utilized in many countries. Products from this tree are obtained from the leaves, the sap, fruits, and stalk. Young shoots, decayed wood and its roots or leaves find use as medicine in various parts of south Asia for herpes, toothache, and head ache. The sap is a source of sugar about 14-17% of sucrose and organic acid which used to produce vinegar and alcoholic beverages in Phillipines and Malaysia (Halos, 1981).

Figure 1.1: *Nypa Fruticans*

Corrosion inhibitor is a chemical compound that is used for the purpose to decrease the corrosion rate of a material, typically metal or alloy. The mechanism for inhibiting corrosion involves formation of a coating which prevents access of the corrosive substance to the metal. Inorganic inhibitors, which are mainly oxidizing agents, such as chromates, iodates, and tungstate act as anodic inhibitors and their metallic atoms are enclosed in the film improving its corrosion

resistance. Unfortunately these compounds are very expensive. Although many of these tested compounds have high inhibition efficiencies, the usage of them still undesired due to their adverse effect on human, environment, as well of their high cost. The increasing concern about these problems had attracted industries to replace it with more environmentally acceptable, readily available and renewable source for wide range of inhibitors which have rich source of ingredients and have very high inhibition efficiency. The corrosion inhibition activity in many plant extracts could be due to the presence of heterocyclic constituents like alkaloid and flavonoid. Present of tannin, cellulose and polycyclic compound could enhance the film formation over the metal surface, thus aiding corrosion (Raja P B and Sethuraman M G, 2008).

1.2 Problem Statement and Motivation

Malaysia has been one of the most extensive natural gas pipeline networks in Asia since the Peninsular Gas Utilization (PGU) project had been completed in 1998. PGU systems can transport the capacity of 2 billion cubic feet per day (Bcf/d) of natural gas (Energy Information Administration, 2011). Currently, Malaysia has over 2,554 km of natural gas pipeline across the country. This pipeline was monitoring by Petronas Gas Berhad (PGB) operating division that is Transmission Operating Division (TOD) for over 24 years and had shown the great achievement in pipeline safety (Mohd Nazmi, 2008). The condition of the pipeline and its railways must always been inspect to ensure the pipeline does not have any leaking or damages.

Even though the damages of pipeline could cause from many aspects, but in this research, we will discuss more on the corrosion part. Naturally the corrosion happen on all types of material but it was had been most commonly associated with metals. Metals corrode because we use them in environments where they are chemically unstable. Only copper and the precious metals (gold, silver, platinum, etc.) are found in nature in their metallic state. The high risk of corrosion attacks on pipeline was become more serious as the pipelines were used for decade to transporting the chemical, liquid or gas. Pipelines that was buried underground transport whether crude oil, gas or water will across various environment such seawater (offshore) and soil (onshore) that may lead into the corrosion attack and finally leaking situation.

The corrosion of pipelines will cost huge amount of money to repair it and will brought the huge lost to the government. The study of efficient and economical natural corrosion inhibitor is necessary to avoid more losses and hazardous condition. Corrosion of pipeline will lead into

leaking and also rapture of it that very unsafe to the environment especially human being as these pipelines may across their neighbourhood. This hazardous situation can inflict human fatality and also badly damage the environment, assets, and even human as the substances that had been transport using the pipelines was highly in pressure (Hopkins, 1995; National Energy Board, 1996; Yahaya *et al.*, 2009). Therefore, this study was conducted to find new environmentally safe, readily available and economic corrosion inhibitors and also the efficiency of the inhibitor.

1.3 Research Objective

The objective of this research is to study the inhibition performance of Nypa fruticans Wurmb as a corrosion inhibitor for carbon steel in acidic solution.

1.4 Scope of Research

The following are the scopes of this research:

- Study of inhibitory efficiencies (%I.E) through weight loss of the steel.
- Study of the parameter that could influence the performance of the inhibitor:
    - Concentration of the inhibitor
    - Acidic pH value of the solution.

1.5 *Main Contribution of This Work*

This study will give benefits to industries that involves with piping system by reducing the cost of maintenance in order to reduce the corrosion rate of the pipeline. As the raw material (Nypa Fruticans) to produce this inhibitor is abundance around this country and the process to produce it is simple, it is assumed that the cost of this natural corrosion inhibitor will be cheaper compare to the cost of other commercialize inhibitor. Moreover this inhibitor gives no harm to human and is environmentally friendly. The Environmental Risk Management Authority on its own initiative had issued a Group Standard named Corrosion Inhibitors (Subsidiary Hazard) Group Standard 2006 under pursuant to section 96B of the Hazardous Substance and New Organisms Act 1996 (HSNO Act, 1996). This proves that commercialize corrosion inhibitor is hazardous and the safer way is by using the natural corrosion inhibitor.

2 LITERATURE REVIEW

2.1 General Overview

The use of corrosion inhibitor is one of the practical methods to reduce the corrosion rate. The inhibitors used for the control of corrosion for metals and alloys which are in contact with aggressive environment is still an accepted practice. It can be used to prevent metal from corrosion in corrosive media and decrease hydrogen evolution. Large numbers of organic compounds were studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings (P.B Raja, M.G Suthuraman, 2008). It is a need to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients with very high inhibition efficiency. As a result, corrosion inhibitors for hydrochloric acid, phosphoric acid and sulphuric acid have attracted increasing attention due to their extended applications.

Many researchers have been conducted to investigate natural corrosion inhibitors. One of the techniques is by using water extract from leaves of certain plant. In one of the study on leaves of economic plants, water extracts from leaves of date palm, *Phoenix dactylifera*, henna, *Lawsonia inermis*, and corn, *Zea mays*, were tested as corrosion inhibitors for steel, aluminium, copper and brass in acid chloride and sodium hydroxide solution using weight loss, solution analysis and potential measurements. The inhibition action was critically depending on metal type and solution composition. Only date palm and henna extract were found highly effective in reducing corrosion rate of steel in acid chloride solution and aluminium in sodium hydroxide solution. The inhabitation increase with the concentration of the plants extract. According to Temkin isotherm the inhibition was interpreted in terms of chemisorptions of some active ingredients in the leaves.

2.2 Nypa Fruticans Wurmb as Corrosion Inhibitor

Nypa Fructican Wurmb is one of the potentially economical, available, non-toxic, and environmentally safe for the research of corrosion inhibitors. It is planted as substituent for mangrove tree for the purpose of agriculture. Various parts of the tree have been use in many ways around Asia. The sap from N. fruticans tree contains mainly succinic acid. The syrup tapped from the stalk is red and its solids contain 83.67% sucrose and 2.27% reducing sugar (A. Tomomatsu et al, 1996).

Previous research proves that Nypa Fruticans Wurmb could serve as an effective inhibitor of the corrosion. Weight loss and hydrogen gas evolution techniques were used to determine the inhibition properties of Nypa Fruticans leaves extract. The maximum inhibition efficiency and surface coverage was obtained at an optimum concentration. The increase in temperature decreased the inhibition efficiency at the temperature range studied. The inhibition action of Nypa Fruticans Wurmb was compared closely to that of 1, 5 Diphenyl Carbazone (DPC). Highest inhibition efficiency for zinc in the present of Nypa Fruticans Wurmb extract was 75.11% and 70.18% with DPC at 30^{o}C. The result showed that the leaves of Nypa Fruticans Wurmb could serve as an effective corrosion inhibitors of mild steel in hydrochloric acid media (K.O. Orubite, N.C. Oforka,2003).

2.3 Material Preparation

N. fruticans leaves extract used as additives to HCl solutions was obtained by drying the leaves for 3hours in an oven at 100 ^{o}C. the leaves is then is grinded to powdery form. A 10-g sample of the powder was dissolved in 500 ml of methanol and left standing for 48 h with occasional shaking. Thereafter, the solution was filtered and the methanol left to evaporate. Dark brown sticky residue was obtained. (K.O. Orubite, N.C. Oforka,2003).

Mild steel will be used to test the inhibition performance of the N. Fruticans Inhibitor. Previous research use sheets of mild steel obtained locally and of 1-cm thickness were mechanically precut into 5x4 cm components. Each coupon was perforated with a hole of the same diameter at the side to allow the passage of a hook. The metal coupons were mechanically cleaned and scrubbed with sand paper to expose clean shining surfaces and degreased in absolute ethanol. They were then dipped into acetone and finally placed in a furnace at a temperature of 40 ^{o}C for 15–20 min. They were allowed to cool overnight in a desiccators before weighing using a

Mettler balance model AE166. All of the steel coupons used in this study will be prepared according to the American Society of Testing Material (ASTM) standards (ASTM G1-90, 1992: ASTM g1-72, 1993).

2.4 Performance Evaluation Technique

Corrosion coupons not only provide information on metal loss and corrosion rate but also on the distribution and forms of corrosion. Technical standards for corrosion testing include ASTM G1 for metal loss calculation. The basic analysis will be done is weight loss measurement for each coupon steel. The weight loss technique will be evaluated as the difference in the weight of the steel coupons before and after the test. It will be determined using this equation:

$$\mathbf{W = (W_i - W_f)\ g} \qquad \textbf{Eq. (2.1)}$$

Where W_i is the initial weight of coupon and W_f is the final weight of the coupon after experiment (Orubite-Okorosaye. k, 2004). The weight of the sample before and after corrosion process will be recorded to determine the corrosion rate.

The inhibition efficiency (%I.E) of a substance is estimated by comparing the corrosion rate in the presence and in the absence of that substance:

$$I.E\% = \left[1 - \frac{W_1}{W_2}\right] x100 \qquad \textbf{Eq. (2.2)}$$

Where W_1 and W_2 are the weight losses for coupon n the presence and absence of Nypa Fructicans Wurmb additive respectively in HCl at same condition. (Ekpe et al, 1994).

Standard deviation measures the amount of variation or dispersion from the average value. A low standard deviation indicates that the data points tend to be very close to the mean value.

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \qquad \textbf{Eq.(2.3)}$$

Where S is standard deviation, X is each value in data set, $\bar{X}$ is the mean or average value, and n is the number of values in the data set.

Box plot is a convenient way of graphically presenting group of data. Data like Minimum, Upper Quartile, Median, Lower Quartile, and Maximum data could be observed through the graph. The calculation and graph designing were made in Microsoft Excel.

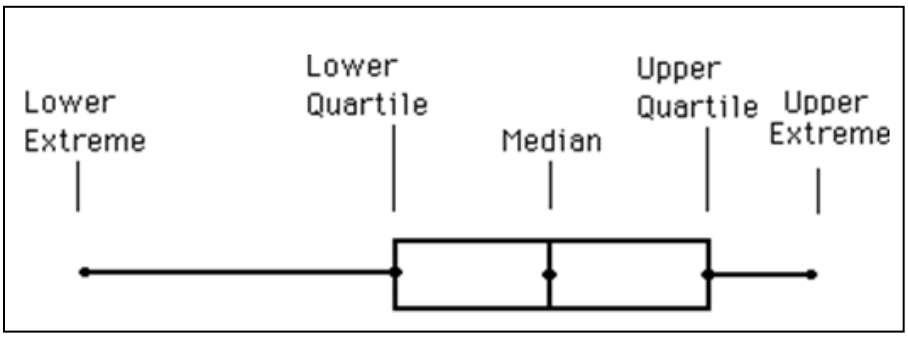

Figure 2.1: Example of Box Plot.

3 MATERIALS AND METHODOLOGY

3.1 Material Used

3.1.1 Nypa Fruticans Wurmb

Nypa Fruticans Wurmb leaves was collected from rural area at Kuantan, Pahang. The leaves were washed and dried in oven for 3 hours at 100^{o}C. Then it was grinded to powdery form. 30g of the powder were added into 200ml of 90% methanol in 500ml volumetric flask and left to stand for 48 hour for occasional shaking. Then the mixture was filtered using filter paper in order to remove the filtrate and the methanol solution was left evaporated to dryness in fume hood. Dark brown sticky solid residue formed at the bottom of the beaker. It was then carefully collected and used as inhibitor for this study.

Figure 3.1: Nypa fruticans powder.

Figure 3.2: Dried Nypa Fruticans extract (Inhibitor).

3.1.2 Steel Coupons

Carbon steel coupon was used in this study. All coupons were prepared according to the ASTM standards (ASTM G1-90, 1992: ASTM g1-72, 1993). These coupons were cleaned using grinder machine in order to make sure that the surface of these steel coupons are completely smooth and free from any past corrosion process. After that the coupons were degreased using ethanol and dipped into acetone. Then it was placed in furnace at temperature 40^{o}C for 15-20 minutes to make sure it was completely dry for weighing process. Each coupon was weighed to obtain the initial weight before the weight lost experiment started.

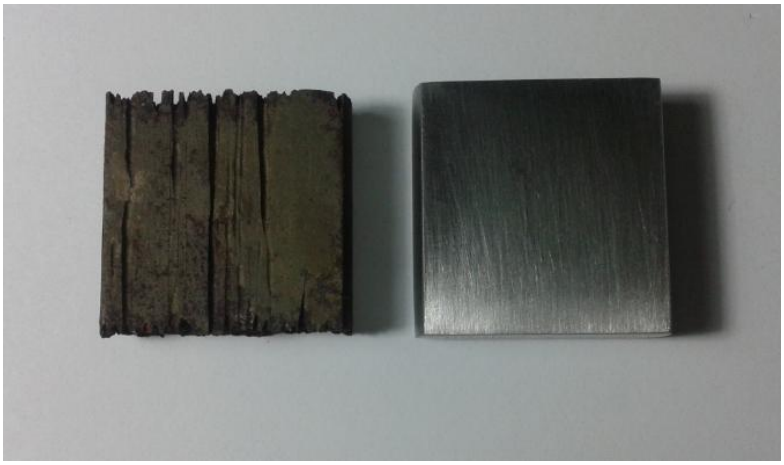

Figure 3.3: Difference between corroded and clean steel coupon.

Figure 3.4: Grinder machine.

3.1.3 Chemicals

Chemicals used in this experiment come from supplier which is ordered under the name of Chemical Lab Technical Unit, Universiti Malaysia Pahang (UMP). Hydrochloric acid, ethanol, and acetone are the only chemical needed for conducting this experiment.

Table 3.1: List of chemicals and its functions

Chemicals	Function
Hydrochloric Acid	For the solution preparation
Methanol	Act as solvent to extract Nypa Fruticans powder
Acetone	Act as cleaning agent for the steel coupons

3.2 Experimental Procedures

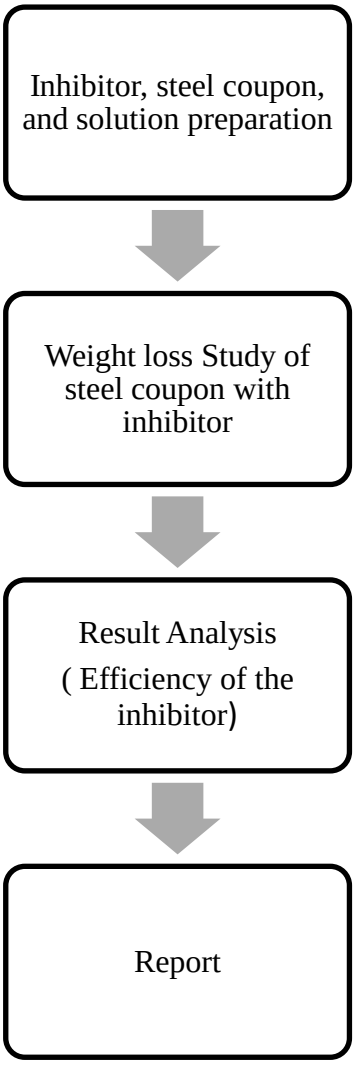

Figure 3.5: Experimental Procedure

3.2.1 Solution Preparation

The Explanation of preparation on the inhibitor and coupon steel has been covered in 3.1. For the solution preparation, the solutions were prepared according to the scope of this study. There were 9 test conditions were made in this study and each test condition contain 3 sets of solution and steel coupons so that more accurate result could be obtained by calculating the average results from the experiment. 0.1 g of the brown sticky Nypa Frutican inhibitor was dissolved in 100ml of 0.1M of HCl to produce an inhibitor concentration of 0.001 g/ml. The solution was stirred using magnetic stirrer to make sure that all inhibitor was completely dissolve. After that, the concentration of 0.000, 0.0025, 0.005 g/ml inhibitor was prepared. For the test of different concentration of HCl, 0.0025 g/ml inhibitor solution was prepared using 100 ml of 0.05M and 0.001M HCl. Another set of same molarity of HCl but without any inhibitor in it was prepared as blank to compare the weight loss with and without inhibitor.

Figure 3.6: Inhibitor solution in HCl

3.2.3 Weight loss study

Weight loss experiment was carried out using 30 glass containers which can contain liquid up to 150ml. A few small holes were made at the top lid of the container to allow air flow into the container for the corrosion process to occur. The 100ml solution prepared was poured into this container carefully. Then a cleaned and weighed steel coupon was immersed carefully into the solution at bottom centre of the container. The container then was closed using its lid to avoid any other contaminant. The coupons were retrieved after 7 days of the experiment. Each retrieved coupon were washed several times with the aid of a soft brush, cleaned and dried in acetone. Further drying was done in a furnace at 40 ^{o}C for 15–20 min. The steel coupons were weighed again in order to obtain the final weight after they were cooled. The weight loss was then evaluated.

Figure 3.7: Glass container and it's lid.

Figure 3.8: Corroded steel coupons after 7 days of the experiment.

3.2.5 Result analysis

The basic analysis done was weight loss measurement for each steel coupon retrieved. The weight of the steel coupons before and after corrosion process was recorded to determine the corrosion rate. The weight loss technique was evaluated as the difference in the weight of the steel coupons before and after the test. It was determined using Eq. (2.1). Standard deviation was then calculated to make sure that the data obtained is in a close range by using Eq. (2.3). Then the average weight loss for each set condition was determined in order to get more accurate result. The inhibition efficiency percent, (%I.E) was estimated by comparing the corrosion rate in the presence and in the absence of the corrosion inhibitor using Eq. (2.2)**.** All data and result obtained were recorded in Table 4.1, Table 4.2, and Table 4.3. Graph were plotted to summarise the result of this study.

4 RESULT AND DISCUSSION

4.1 Corrosion of Mild Steel in Various Concentration of Inhibitor

Table 4.1: Weight loss study on various concentration of inhibitor in 0.1M HCl.

Test	Inhibitor Concentration (g/ml)	Steel Coupon	Initial Weight, W_i (g)	Final Weight, W_f (g)	Weight Loss, W_L (g)	Average Weight Loss, Avg W_L (g)	Standard Deviation	Inhibition Efficiency I.E%
1	0.0000	1	40.8221	29.6474	11.1247	11.5547	1.33	-
		2	42.0134	31.5207	10.4927			
		3	41.8903	28.8435	13.0468			
2	0.0010	1	41.4278	36.1514	5.2764	5.6016	0.78	51.52
		2	40.8966	34.4069	6.4897			
		3	40.5763	35.5375	5.0388			
3	0.0025	1	40.4080	35.2387	5.1693	4.6244	0.52	59.98
		2	41.7423	37.1745	4.5678			
		3	41.5337	37.3976	4.1361			
4	0.0050	1	40.9341	36.2591	4.6750	3.8273	0.74	66.88
		2	40.8468	37.5493	3.2975			
		3	41.0962	37.5859	3.5093			

From the result in Table 4.1, the average weight loss of steel coupons of 0.000 g/ml shows the highest value which is 11.5547 g because there were no inhibitors in the solutions. The inhibition efficiency was calculated using the value obtained from the average weight loss. Solutions with 0.001, 0.0025, and 0.005 g/ml give lower average weight losses which are 5.6016, 4.6244, and 3.8273 g and higher percentage of inhibition efficiency which are 51.52 %, 59.98 %, and 66.88 %.

4.1.1 Weight loss of steel coupons after 7 days exposure to Inhibitor-HCl solutions.

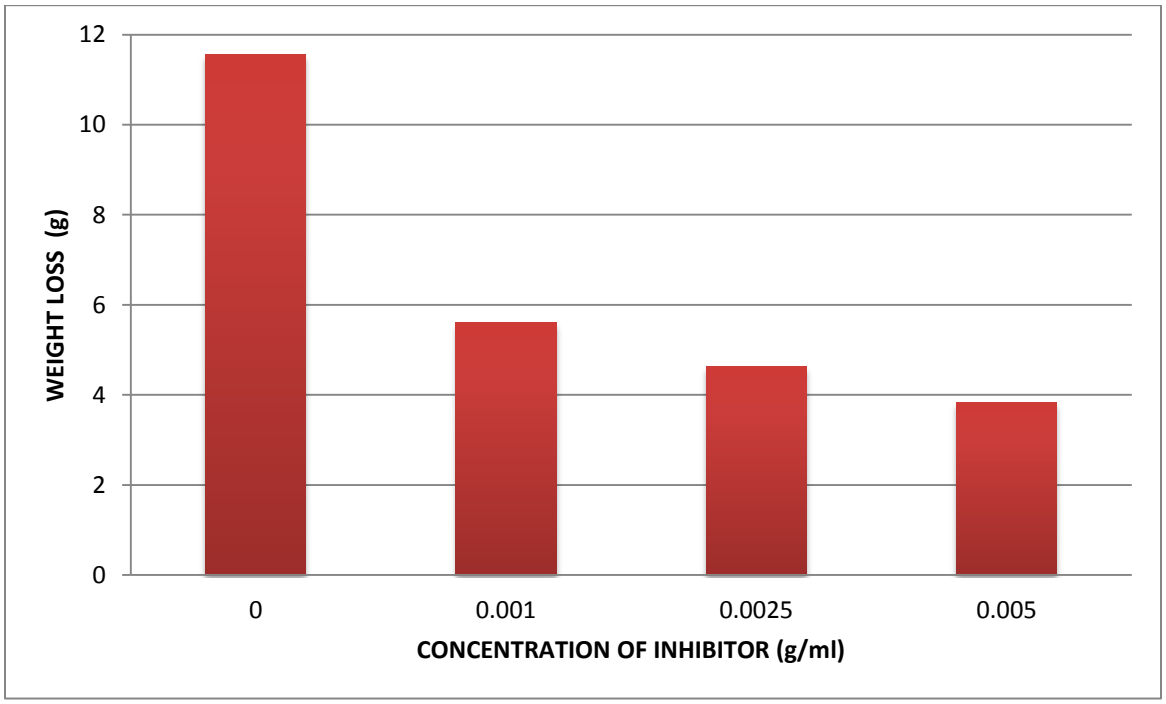

Figure 4.1: Result of weight loss of steel coupons in various concentration of inhibitor.

Figure 4.1 show the trend of average weight loss of steel coupons with the increase of Nypa Fruticans Inhibitor. From this graph, it can be conclude that the weight loss of steel coupons decrease when the concentration of the inhibitor increase. Big different can be observe between weight loss of the steel coupons with inhibitor and without any inhibitor. This proves that the extract from Nypa Frutican's leaves can act good natural corrosion inhibitor.

4.1.2 Worse Case Scenario

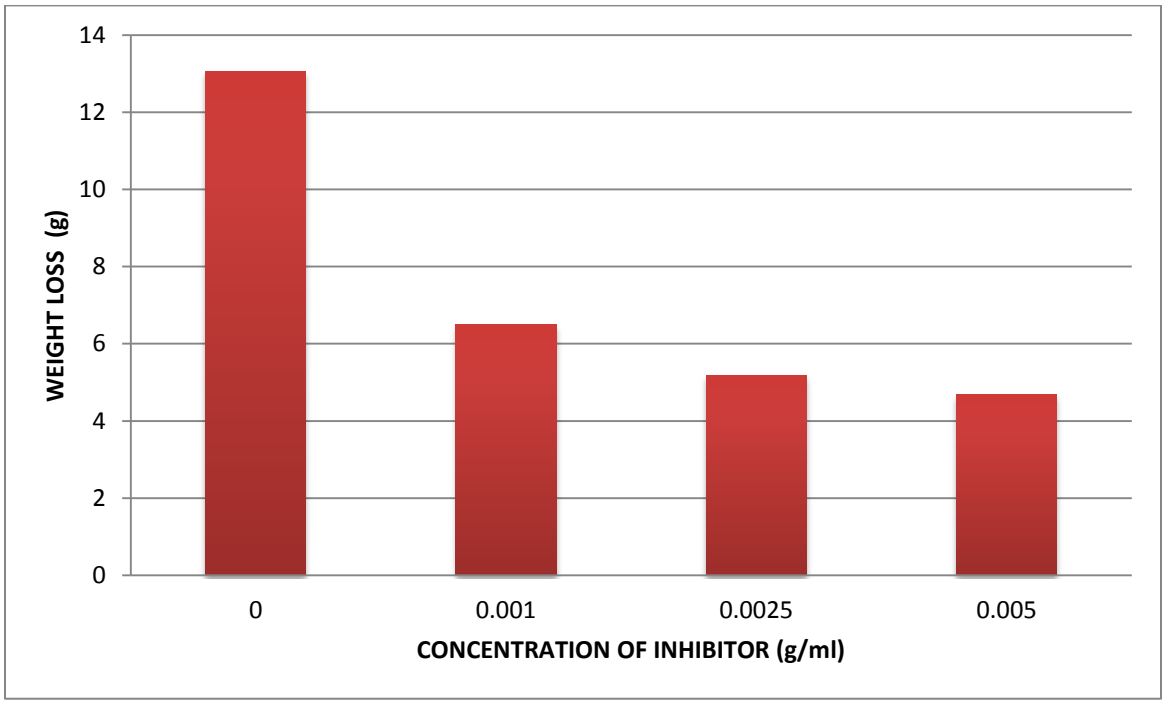

Figure 4.2: Worse case scenario for weight loss of steel coupons in various concentration of inhibitor.

Graph for worse case scenario for weight loss of steel coupons after 7 days of exposure in various concentration of inhibitor in 0.1M HCl was plotted in Figure 4.2. This data was plotted according to the highest data from each set of test in Table 4.1. Even with the highest data, the trend of this graph is the same as in Figure 4.1 which conclude that the higher the concentration of inhibitor in the HCl solution, the lower is the weight loss of the steel coupons.